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TIN SALTS IN CANNED FOODS OF LOW ACID CONTENT, WITH SPECIAL REFERENCE TO CANNED SHRIMP.

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INTRODUCTION.

It is customary to attribute the presence of tin salts in canned foods to the action of the acids of those foods on the tin of the container. We usually think of the action of a food upon the tin as proportional to the acidity of the food.

The acidity of many products ordinarily preserved in cans is so high and their effect on the tin lining of the container so marked as to offer a sufficient explanation of the amount of tin salts they contain, and until recently the high tin content of certain vegetables and other products of low acidity was overlooked or regarded as accidental. The interest lately awakened in the subject of tin salts has led to a more careful study of the question than has been given it before and it is now recognized that several articles such as certain varieties of fish, beets, lima beans, asparagus, and pumpkin, though being almost without acidity, have a marked solvent action upon the tin lining of the container in which they are preserved. As far as we are aware, however, no explanation of this fact has been offered.

TIN CONTENT OF CANNED GOODS VARYING IN ACIDITY AND AGE.

The relation of the acid to the tin content of a series of canned goods, examined about six months after they were packed, is well shown by the following table in which the acidity is expressed as acetic acid and the amount of tin is stated in milligrams per kilogram

of the canned food and as milligrams of tin for each 100 mg of acid. In the table those foods having the highest amount of tin in relation to their acidity are given first, and it is seen that the fruits whose action on tin is most familiar to us because of their high acidity come last in the list with from 1 to less than 5 mg of tin per 100 mg of acid.

TABLE 1.—*Acidity and tin content of canned goods about six months after packing.*

Substance.	Acidity as acetic acid.	Milli-grams of tin per kilogram.	Milli-grams of tin per 100 milli-grams of acid.	Substance.	Acidity as acetic acid.	Milli-grams of tin per kilogram.	Milli-grams of tin per 100 milli-grams of acid.
	Per cent.				*Per cent.*		
Salt fish	0.012	90	75.0	Peas	0.126	57	4.5
Do	.012	112	93.3	Do	.025	13	5.2
Beets	.036	262	72.8	Pears	.180	86	4.8
Corn	.012	33	27.5	Do	.180	79	4.4
Do	.012	46	38.3	Raspberries	.450	174	3.9
Pumpkin	.072	193	26.8	Tomatoes	.390	290	7.4
Lima beans	.017	36	21.2	Do	.390	145	3.7
String beans	.108	80	7.4	Do	.234	84	3.6
Do	.108	98	9.1	Cranberries	.534	180	3.3
Pumpkin	.156	117	7.5	Cherries	.966	146	1.5
Do	.156	93	6.0	Peaches	.486	90	1.9
Corn	.019	12	6.3	Grapes	.510	61	1.2
Peas	.126	69	5.5	Plums	.582	63	1.1

In some of the vegetables considered in this table the ratio of tin to acid is a little higher than in the case of some of the fruits shown. It is distinctly higher in all cases, however, especially if the pears, which are somewhat anomalous in one other respect, are excluded. Moreover, in the fish and in a number of the vegetables the ratio of tin to acid is strikingly higher than in the fruit. In a general way the ratio of tin to acid in the fruits appears to depend on the variety of the acid the fruit contains, the solvent action of citric acid, to which the acidity of raspberries and tomatoes is due, being less than that of malic acid. Pears appear to be an exception to this rule, however, since, notwithstanding the fact that their characteristic acid is malic, they contain a greater amount of tin in proportion to their acidity than any of the other fruits.

It is obvious that in data of this kind conclusions must be drawn from the data as a whole rather than from the analyses of individual cans. For instance, one of the samples of tomatoes has 7.4 mg of tin for each 100 mg of acid, whereas the second sample, put up at the same time and from exactly the same batch of tomatoes, but in a different kind of plate, contains but 3.7 mg of tin for each 100 mg of acid. A wide difference is shown also among the samples of corn and of pumpkins examined. The general trend of the results is so striking, however, as to indicate that individual differences may be over-

looked for the present and can not be regarded as overthrowing the generalization that the products given first in Table 1 contain some substance other than acid that has a marked solvent action on tin.

Table 2 gives the results obtained in the examination of a series of samples of unknown origin, but whose age is known to be at least as great as that stated. In general the results given therein are similar to those shown in Table 1.

TABLE 2.—*Acidity and tin content of old canned goods.*

Substances.	Average age of sample in years.	Acidity as per cent acetic acid	Milligrams tin per kilogram.	Milligrams tin per 100 milligrams acid.
Yellow beets	Over 3	0.05	725	145
String beans	Over 10	.04	551	138
Corn	10	.11	563	51
Succotash	Over 3	.10	444	44
Mock turtle soup	Over 5	.10	306	30
Asparagus	2 to 3	.13	333	26
Tomatoes	16	.48	944	20
Peaches	Over 3	.43	786	19
Apples	Over 5	.22	364	17
Red kidney beans	Over 10	.23	313	14
Blackberry jam	8	.31	383	12
Roast beef	Over 10	.33	426	11
Beans (baked)	18	.34	388	11
Apricots	Over 3	.49	487	10
Lima beans	8	.19	170	9
Green gages	Over 3	.69	519	8
Apple butter	Over 5	1.05	690	7

STUDY OF CANNED SHRIMPS.

It is evident from these tables that in a study of the tin salts present in canned foods there is some important factor besides their acidity. It was thought that some light might be thrown upon this subject by the study of canned shrimps. It is recognized by packers that shrimps contain some corrosive substance which greatly interferes with their handling and preservation. It attacks the workmen's hands, causing the skin to peel, and also eats through the leather of their shoes. Tins in which the shrimps are preserved are quickly perforated. Packers have found that this substance seems to disappear when the shrimps are preserved with ice. Ordinarily they are caught at some distance from the packing houses and iced in the boats, so that by the time they reach the packer their corrosive property has disappeared to such an extent as to make it practicable to work with them. When caught near the packing house it is now customary to lay them down with ice for a day or so, during which time they lose this corrosive property.

There were recently received at this laboratory from A. W. Bitting several cans of headless shrimps—that is, shrimps from which the heads have been removed but not the shells—procured by him and packed in his presence at Biloxi, Miss. It was found that they con-

tained a volatile alkaline substance, apparently monomethylamin, which attacks tin quite markedly and which also attacks the skin of the hands. From the volatile nature of the alkali it seems possible that the portion of it on the surface of the shrimp may escape when the shrimps are preserved on ice for a time and so explain the fact that shrimps so treated do not attack the skin. Even when so treated, however, special precautions must be taken to protect cans in which shrimps are preserved. Ordinary tin containers employed for the preservation of shrimps are rapidly corroded and the lining completely removed. To prevent this the cans are lined with parchment paper and corrosion is then only noted at the junction of the papers and at points where for some reason the paper is pressed against the tin coating. As the points of junction of the paper leave a free opening the reason for the attack there is self-evident. The attack at places where the paper is pressed against the can is believed to be due to surface action. The liquor separated from the shrimps was found to be alkaline to litmus. The alkalinity was measured as follows:

50 grams of this liquor required 8.1 cc of tenth-normal hydrochloric acid to make it neutral to azolitmin;

50 grams of this liquor required 44.5 cc of tenth-normal hydrochloric acid to make it neutral to methyl orange;

50 grams of this liquor required 15 cc of tenth-normal sodium hydroxid to make it neutral to phenolphthalein.

These results show that this liquor contains quite a large quantity of a moderately weak base partlyl combined with a weak acid, and hence largely hydrolyzed to contain considerable numbers of hydroxyl ions.

Some shrimps were extracted with alcohol and the volatile alkali distilled over as given below. This alkali was just neutralized with hydrochloric acid and the resulting solution evaporated to dryness on a steam bath. In the white, crystalline, deliquescent salt so obtained chlorin and nitrogen were determined with the following results:

TABLE 3.—*Analysis of the volatile alkali.*

Determinations.	Found.	Calculated for $N(CH_3)H_3Cl$.
Chlorin	52.0	52.5
Nitrogen	21.4	20.9

The chlorplatinate of this amin was found to consist of bright yellow crystals containing 41.9 per cent of platinum. The theoretical amount in $(N(CH_3)H_3)_2PtCl_6$ is 41.3 per cent.

Twenty cans of shrimps were ground up, covered with alcohol, and allowed to extract for two days. The extract was passed through muslin and the filtrate made slightly acid with sulphuric acid and evaporated to a small volume. To this extract magnesium oxid was added in excess and the volatile alkali distilled. The distillate, which smelled much like ammonia, was just neutralized with sulphuric acid and alcohol was added, causing the separation of a crystalline precipitate.

This was dissolved in water and reprecipitated with alcohol, giving 6 grams of dry salt. Some of this salt was distilled with sodium hydrate, the distillate (marked Solution I) was made up to such a volume that it was a deci-normal alkali, and its solvent action on tin was determined. When this solution was boiled for one hour with two plates of thin block tin, each 2 by 3 inches, 6 mg went into solution from each plate. Another portion of the solution, after neutralization with hydrochloric acid, was boiled in the same manner and dissolved 5.8 mg from each plate. A tenth-normal solution of methylamin treated in the same manner dissolved 5.7 mg of tin from each place. Similar plates were boiled for one hour in dilute solutions of other alkalis, amins, and amino acids, including one of the purin bases, with the following results:

	Mg per plate.		Mg per plate.
Sodium hydroxid, tenth-normal	5.0	Aspartic, 0.3 per cent	3.7
Potassium hydroxid, tenth-normal	7.5	Alanin, 0.3 per cent	2.4
Ammonium hydroxid, tenth-normal	1.3	Glycocoll, 0.3 per cent	3.3
Sodium hydroxid, fourth-normal	6.2	Sarkosin, 0.3 per cent	5.0
Acetamid, 2 per cent	6.5	Tyrosin, 0.3 per cent	2.4
Asparagin, 3 per cent	4.4	Hypoxanthin, 0.3 per cent	4.2
Asparagin, 0.3 per cent	4.3	Creatin, 0.3 per cent	2.9
		Leucin, 0.3 per cent	1.7

DETERMINATION OF VOLATILE BASES IN OTHER COMPARATIVELY NONACID FOODS.

It appears, therefore, that monomethylamin exists to a considerable extent in shrimps, and explains largely their corrosive action on tin containers. The thought suggests itself that the solvent action of certain other nonacid or slightly acid foods may be explained in the same manner, and that amins and amino acids as a class may have a marked solvent effect on tin. These bodies are known to be present in practically all fish. According to Schreibler,[1] beets contain 0.25 per cent of betain and ripe beets 0.10 per cent. Asparagin has been found in asparagus, several vetches, beets, beans, and sometimes in peas. Although asparagin is formed especially during the germination of these products, it is also present in the unripe vegetables. Among

[1] Ber. d. chem. Ges., 1870, 3 : 155.

the vegetables which are recognized as strongly attacking tin containers are asparagus, spinach, string beans, and pumpkin. Samples of these substances of unknown history were procured and the acidity to phenolphthalein, the measure of amino acid by titration after adding formaldehyde (Sorensen's method), alkalinity to methyl orange, and total volatile alkali were determined in each case. The results are given in the following tabular statement calculated for 100 grams of sample. It is suggested that these volatile alkalis and amino acids are responsible to a great degree, if not entirely, for the solvent action on tin exerted by foods of very low acidity.

Volatile bases in canned goods.

Determination.	Asparagus (can badly corroded).	Spinach (can badly corroded).	String beans (can but little corroded).	Pumpkin (can badly corroded).
(1) Titration to phenolphthalein (cc N/10 NaOH)	20.0	20.0	12.0	20.0
(2) Same as (1). Calculated as per cent of acetic acid	.12	.12	.07	.12
(3) Titration after adding 10 cc formaldehyde to the neutral solution (cc N/10 NaOH [1])	32.0	23.0	29.0	24.0
(4) Same as (3). Calculated as per cent of aspartic acid	.43	.31	.38	.32
(5) Titration to methyl orange (cc N/10 HCl)	13.0	29.0	13.0	28.0
(6) Volatile alkali, titration to methyl orange (cc N/10 HCl)	9.7	6.7	4.0	7.7

[1] Corrected for the acidity of formaldehyde.

It is evident that the volatile alkalis and amino acids which occur in these vegetables probably have an effect on the tin container analogous to that of the methylamin found in shrimp. Further work on this subject is in progress, but, considering the number of chemists who are studying the content of tin salts in canned goods, it seemed best to offer this preliminary statement for the purpose of bringing to the attention of other workers certain phases of tin corrosion which seem to be of considerable importance and which have not been recognized heretofore. Acknowledgment is made to F. W. Liepsner and C. W. Clark for much of the analytical work done in connection with the investigation.

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